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The suitability of the Boltzmann equation for calculating transport coefficients of partially ionized gases is discussed. Analytical and experimental investigations are cited to show that it can be used as a starting point to calculate the total thermal conductivity. The Chapman-Enskog solution of the Boltzmann equation is used to derive an expression for the total thermal conductivity, composed of three parts the translational, reactive, and thermal diffusive components. The reactive and thermal diffusive components are explicitly expressed in terms of the multicomponent and thermal diffusion coefficients. Effects of higher order Sonine expansion terms are examined for the various transport coefficients. The first three orders of the Sonine expansion terms are required for the accurate calculation of the translational thermal conductivity, whereas only the first two orders are sufficient for the calculation of the multicomponent and thermal diffusion coefficients. These diffusion coefficients are then used to calculate the reactive and thermal diffusive components of the total thermal conductivity of hydrogen, nitrogen, and argon at conditions where the reactive component is at a maximum. These values of the reactive conductivity are examined to determine the relative importance of multicomponent and thermal diffusion. The predominant mechanism for hydrogen is the binary diffusion of atoms and ions, although the effects of thermal diffusion of electrons is also important. Thermal diffusion becomes more dominant as the molecular weight of the atom increases. In fact, the multicomponent diffusive effects for argon cancel, and the reactive thermal conductivity can be attributed almost entirely to the thermal diffusion of electrons.

Key Words: Boltzmann equation, Chapman-Enskog formulation, ionized gases, multicomponent diffusion, thermal conductivity, thermal diffusion.

1. Introduction

An object traveling through an atmosphere has part of its kinetic energy converted into thermal excitation of the surrounding flow field gas molecules. When the speed is sufficiently high, the gas decomposes into a complex mixture of molecules, atoms, ions, and electrons. The total thermal conductivity of this gas must be known in order to determine the heat flux into the surface of the object. In the calculation of the thermal conductivity of this ionized gas, one would ask the following questions. First, does the presence of charged particles introduce phenomena which affect the thermal conductivity? Second, is the theory which is used for neutral gases sufficiently general to account for these phenomena? This paper will describe some of the analytical and experimental work done in the past few years to resolve these two questions.

The greatest difference between an ionized gas and a neutral gas lies in the range of intermolecular forces. For example, the effective range of the force between two neutral particles or a charged particle and a neutral particle is orders of magnitude smaller than the average intermolecular spacing. These effective ranges are in accord with the basic assumption that particle collisions in the gas are binary a necessary condition for the validity of the Boltzmann equation governing the transport coefficients of neutral gases. In contrast, the effective range of the intermolecular forces between two charged particles is usually greater than the average intermolecular spacing. At first appearance, this suggests

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that the Boltzmann equation is not valid for gases with an appreciable degree of ionization. This situation prompted Spitzer and his coworkers [1 and 2]³ to derive a theory which describes transport phenomena (specifically electrical and thermal conductivity) of an electron gas where the interactions are attributed to many long-range simultaneous but <u>independent</u> Coulombic interactions. The collision term in the Boltzmann equation was replaced by the Fokker-Planck expression which describes these simultaneous interactions. Recently Gross [3], Grad [4], Koga [5], and others re-examined the mathematical implications of the Boltzmann and Fokker-Planck equations and concluded that the Boltzmann equation was valid for ionized gases after all. Grad stated that

". . .The critical point here is that, although the two physical pictures are entirely different, their mathematical descriptions are identical! The net effect of many successive independent small impulses is the same as many simultaneous independent small impulses, provided only that the means and variances of the two impulse distributions are the same (actually, the entire probability distributions were taken to be the same). Thus we conclude, without setting pencil to paper, that the Fokker-Planck equation, which is an immediate consequence of the simultaneous grazing impulse model, must yield results identical with those obtained from the Boltzmann equation, provided that an appropriate grazing collisions approximation is made and the same cut-off is used in the latter computation."

The equivalence between the Boltzmann and Fokker-Planck equation for the case of a fully ionized gas was further demonstrated by the excellent agreement of the two sets of values of transport coefficients based on these equations [2].

A more rigorous theory for fully ionized gases can be derived from Bogolyubov-Born-Green-Kirkwood-Yvon hierarchy of equations [6] which account for simultaneous but <u>dependent</u> interactions (i.e. many particle correlations). An analysis by Sundaresan and Wu [7] has shown that the thermal conductivity from the B-B-G-K-Y approach is almost identical to that for the Fokker-Planck approach.

The accuracy of the Boltzmann equation was demonstrated in two recent experiments by Emmons [8] and Morris [9]. The goal of their experiments was the measurement of the electrical and thermal conductivity of partially ionized gases. Although the thermal conductivity could not be measured accurately at large degrees of ionization because of the masking effects of thermal radiation, the electrical conductivity was measured. In figures 1 and 2 the experimental values of the electrical conductivity are compared with values based on the Boltzmann equation (second-order Chapman-Enskog formulation). It can be seen that the agreement is fairly good over the entire range of temperatures (degree of ionization ranging from 1 percent at 9000°K to 100 percent at 22,000°K). Since the predominant cross section for the electrical conductivity is the well-verified Coulombic cross section, the agreement shown in figures 1 and 2 is a good indication of the validity of the Chapman-Enskog formulation of the Boltzmann equation for all degrees of ionization. Unfortunately, this is no guarantee that the values of the thermal conductivity can be accurately predicted at these high degrees of ionization since the predominant cross sections (e.g. atom-ion elastic and charge-exchange cross sections) are not known accurately, and since there are different types of diffusional effects present in thermal conduction. This means that measurements of thermal conductivity are still necessary.

2. Derivation of Total Thermal Conductivity

The analytical and experimental work described in the previous section indicate that the Boltzmann equation can be used as a starting point to calculate the total thermal conductivity. The approach described in this paper is the same as the Chapman-Enskog formulation applied to the case of neutral monatomic gas mixtures by Hirschfelder, Curtiss, and Bird [10] and will be examined to determine its suitability for a partially ionized gas. Besides the difference in the range of intermolecular forces a partially ionized gas differs from a neutral gas in two other respects. First, a charge separation field arises because of local differences in the ion and electron concentrations, and second, the ratio of the mass of the heaviest particle to that of the lightest particle increases by at least three orders of magnitude due to the presence of free electrons. A great amount of foresight was used in the derivation of the complete Chapman-Enskog formulation, for there exist terms which account for these two differences. In principle the charge separation field can be calculated since a macroscopic force term is included in the Chapman-Enskog formulation. The much larger mass ratio in partially ionized gases is not really a fundamental difference, but it does mean a re-evaluation of certain computational simplifications which were carried over from the calculation of the thermal conductivity of neutral gas mixtures. For example, it has been customary to discard certain Sonine expansion terms in the translational thermal conductivity and the multicomponent diffusion coefficients, and to omit effects of thermal diffusion on the total thermal conductivity [10]. An examination of thermal diffusive effects does show that the effects are small for neutral gas mixtures, but it also shows that the effects become increasingly important as the

²The Boltzmann approach is presently the only one available for the calculation of transport coefficient of partially ionized gases, although many competing approaches are available for fully ionized gases.

³Figures in brackets indicate the literature references at the end of this paper.

ratio mheavy/mlight increases. Consequently, the author [11 and 12] showed that it was necessary to include the discarded Sonine expansion terms and to include thermal diffusive effects. The results of these calculations will be described in the next section.

The calculation of the total thermal conductivity is based on the expression for the heat flux vector

$$\underline{\mathbf{q}} = \sum_{\mathbf{i}} \mathbf{n}_{\mathbf{i}} \mathbf{h}_{\mathbf{i}} \underline{\mathbf{V}}_{\mathbf{i}} - \lambda_{\mathbf{t}} \frac{\partial \mathbf{r}}{\partial \underline{\mathbf{r}}} - \mathbf{nkT} \sum_{\mathbf{i}} \frac{1}{\mathbf{n}_{\mathbf{i}} \mathbf{m}_{\mathbf{i}}} D_{\mathbf{i}}^{T} \underline{\mathbf{d}}_{\mathbf{i}}, \qquad (1)$$

where D_1^T is the thermal diffusion coefficient, and h_i is the total enthalpy of a particle of species i. The quantity λ_t is the thermal conductivity of a spatially homogeneous gas mixture without concentration gradients. The diffusion velocity, \underline{V}_i , is defined as

$$\underline{V}_{i} = \frac{n^{2}}{n_{i}\rho} \sum_{j} m_{j} D_{i} \underline{j} \underline{d}_{j} - \frac{1}{n_{i}m_{i}T} D_{i}^{T} \frac{\partial \underline{r}}{\partial \underline{r}}$$
(2)

where $D_{i,j}$ is the multicomponent diffusion coefficient and the "forcing potential" for a partially ionized gas in the absence of pressure gradients is defined as

$$\underline{\mathbf{d}}_{i} = \frac{\partial \mathbf{x}_{i}}{\partial \underline{\mathbf{r}}} - \frac{\mathbf{n}_{i} \mathbf{m}_{i}}{\mathbf{p} \rho} \left(\frac{\rho}{\mathbf{m}_{i}} \, \boldsymbol{\epsilon}_{i} \underline{\mathbf{E}}_{i} - \sum_{i} \mathbf{n}_{j} \boldsymbol{\epsilon}_{j} \underline{\mathbf{E}}_{j} \right) \tag{3}$$

where ϵ_i is the charge, Z_i e, for a particle of species i, and \underline{E}_s is the electric field generated by a difference in ion and electron concentrations. Equation (3) differs from the expression for \underline{d}_i in [10] in that $Z_i \in \underline{E}_s$ describes an internal macroscopic force whereas the corresponding quantity in [10] describes an external macroscopic force. However, the conceptual difference is only apparent as \underline{E}_s always stems from an external energy source (e.g. heating coils). Assume that this energy is imposed on the system such that the average temperature is high enough to ionize the gas, but the temperature gradient is small enough to justify linearization procedures. The temperature gradient induces concentration gradients, $\partial_{x_i}/\partial \underline{r}$, and a charge separation field, \underline{E}_s . If it is assumed that both $\partial_{x_i}/\partial \underline{r}$ and \underline{E}_s are proportional to the temperature gradient, it can be seen from eqs (2) and (3) that \underline{V}_i and \underline{d}_i are also proportional to the temperature gradient. The heat flux vector can then be expressed as

$$q = -(\lambda_r + \lambda_t + \lambda_d) \frac{\partial \underline{r}}{\partial \underline{r}} = -\lambda_{total} \frac{\partial \underline{r}}{\partial \underline{r}}$$
 (4)

The reactive component of the thermal conductivity, $\lambda_{\mathbf{r}}$, derives its name because of the addition of the reaction energy to the enthalpy of the individual species [13]. This mode of heat transfer can be described in terms of a diffusion cycle. In the higher temperature region the concentration of ions and electrons are larger than in the lower temperature region, forcing the charged particles to diffuse toward the lower temperature region. In this region, the ion recombines with an electron, thereby releasing the ionization energy (i.e. transport of energy). The cycle is completed when the atom is forced by the atomic concentration gradient to diffuse toward the higher temperature region where the ionization process occurs. The translation component, $\lambda_{\mathbf{t}}$, is the conductivity of a spatially homogeneous gas mixture without concentration gradients, and is the only component explained by simple kinetic theory [10]. For obvious reasons, the third component of the thermal conductivity, $\lambda_{\mathbf{d}}$, is called the thermal diffusive component. Unfortunately, no simple physical picture can describe this mode of heat transport.

The calculation of λ_t is straightforward and is described by Hirschfelder, Curtiss, and Bird [10]. Before numerical values for λ_r and λ_d can be calculated it is necessary to obtain values for the concentration gradient of each species and the charge separation field, all in terms of the temperature gradient. The simplest case which can be examined is that for a gas undergoing the reaction $A \rightarrow I + e$ (i.e. a termary mixture of atoms, A, ions, I, and electrons, e). The solution of the problem can be expressed in terms of four dependent variables - the concentration gradients for the atom, ion, and electron, and the charge separation field, all expressed in terms of the temperature gradient. However, there are only three independent equations relating these four quantities. Two of these equations are statements of the flux conservation of elemental particles as formulated by Butler and Brokaw [13]. For the termary mixture the elemental particles are defined as a singly charged ion and an electron. Then flux conservation requires that the diffusion velocities be related as follows⁴:

⁴More explicit forms of (5) and (6), where \underline{V}_i is expressed in terms of \underline{d}_i , was used in the calculation of [14].

$$x_{\underline{A}}\underline{V}_{\underline{A}} + x_{\underline{I}}\underline{V}_{\underline{I}} = 0, \tag{5}$$

$$x_{A}\underline{V}_{A} + x_{e}\underline{V}_{e} = 0. \tag{6}$$

The third equation can be derived from the expression for the equilibrium constant,

$$K_{p} = \prod_{i=1}^{3} (x_{i}p)^{a_{i}}, \qquad (7)$$

where the a_i 's are the stoichiometric coefficients for the reaction (a_A = -1, a_I = 1, a_e = 1). Combination of the gradient of eq (7) with explicit expressions for the charge separation force results in

$$\frac{\mathrm{d} \ln K_{\mathrm{p}}}{\mathrm{dT}} \cdot \frac{\partial \mathbf{T}}{\partial \underline{\mathbf{r}}} = -\frac{1}{x_{\mathrm{A}}} \, \underline{\mathbf{d}}_{\mathrm{A}} + \frac{1}{x_{\mathrm{I}}} \, \underline{\mathbf{d}}_{\mathrm{I}} + \frac{1}{x_{\mathrm{e}}} \, \underline{\mathbf{d}}_{\mathrm{e}}. \tag{8}$$

The author [12] discussed the difficulties in solving eqs (5), (6), and (8) for $\partial x_1/\partial \underline{r}$ and \underline{E}_s , but could not offer a solution. Subsequently, Meador and Staton [15] circumvented the problem of too many variables by assuming that the concentration gradient of the ion was equal to that for the electron. They justified this assumption by combining concepts from electrostatics and plasma physics with expressions from non-equilibrium thermodynamics, then using order of approximation arguments. The accuracy of this approach will be discussed later. Meador and Staton used the equality of $\partial x_1/\partial \underline{r}$ and $\partial x_e/\partial \underline{r}$ in eqs (5), (6), and (8) to solve for $\partial x_A/\partial \underline{r}$ and \underline{E}_s . Their expression for the reactive component of the thermal conductivity is

$$\lambda_{r} = \frac{n n_{e} n_{A} k T^{2} D_{AI}}{(n_{e} + n_{A})^{2}} \left(\frac{\partial \ln K_{p}}{\partial T} \right)^{2}$$
(9)

which is identical to the Butler and Brokaw expression for dissociating gases [13] if it is assumed that the multicomponent diffusion coefficient D_{AI} can be approximated by the binary diffusion coefficient \mathfrak{D}_{AI} . This equation has several implications: (1) The reactive component is completely dominated by the binary diffusion between the ion and atom, (2) The reactive component is independent of the motion of the electron, and (3) The reactive component is not affected by thermal diffusive effects.

In a subsequent paper [14] the author also derived an expression for the total thermal conductivity. In contrast to the Meador and Staton work, it was not necessary in [14] to rely on any subsidiary assumptions, and the derivation was exact within the framework of the Chapman-Enskog formulation. The crux of this approach is not to separate the forcing potential, $\underline{d_i}$, of eq (3) into $\partial x_i/\partial \underline{r}$ and $\underline{E_s}$ components, but to solve for $\underline{d_i}$ directly by making use of the conservation of the net flux for each elemental particle. Physically, this means that regardless of the value of the charge separation field, the concentration gradients will readjust themselves so that the net flux is conserved (eqs (5) and (6)). Therefore, the combined effects of $\partial x_i/\partial \underline{r}$ and $\underline{E_s}$ in the form of $\underline{d_i}$ is a more logical dependent variable than its components. The solution for the various $\underline{d_i}$'s is then obtained from eqs (5), (6), and (8). The determinantal expression for the various $\underline{d_i}$'s is

$$d_{1} = \frac{\partial T}{\partial \underline{r}} = \frac{\partial T}{\partial \underline{r}} = \frac{a_{12}}{a_{22}} = \frac{a_{23}}{a_{23}} = \frac{-c_{1}}{a_{22}}$$

$$a_{13} = \frac{a_{12}}{a_{22}} = \frac{a_{23}}{a_{23}} = \frac{a_{23}}{a_{23}}$$

$$a_{11} = \frac{a_{12}}{a_{12}} = \frac{a_{13}}{a_{22}} = \frac{a_{23}}{a_{23}}$$

$$a_{21} = \frac{a_{22}}{a_{23}} = \frac{a_{23}}{a_{23}}$$

$$a_{31} = \frac{a_{32}}{a_{32}} = \frac{a_{33}}{a_{33}}$$

$$(10)$$

where

$$\begin{array}{lll} a_{11} &= (n^{2}/\rho) m_{A} D_{IA}, & a_{23} &= (n^{2}/\rho) m_{e} D_{Ae}, \\ a_{12} &= (n^{2}/\rho) m_{I} D_{AI}, & c_{2} &= (D_{A}^{T}/m_{A}T) + (D_{e}^{T}/m_{e}T), \\ a_{13} &= (n^{2}/\rho) m_{e} D_{Ae} + (n^{2}/\rho) m_{e} D_{Ie}, & a_{31} &= -x_{A}^{-1}, \\ c_{1} &= (D_{A}^{T}/m_{A}T) + (D_{I}^{T}/m_{I}T), & a_{32} &= x_{I}^{-1}, \\ a_{21} &= (n^{2}/\rho) m_{A} D_{eA}, & a_{33} &= x_{e}^{-1}, \\ a_{22} &= (n^{2}/\rho) m_{I} D_{AI} + (n^{2}/\rho) m_{I} D_{eI}, & c_{3} &= d \ln K_{p}/dT. \end{array}$$

A combination of eqs (1), (2), (10), and (11) gives the final expression for the total thermal conductivity:

$$\lambda_{\text{total}} = \lambda_{\text{t}} + \left[-h_{\text{I}} \frac{n^{2}}{\rho} (m_{\text{A}} D_{\text{IA}} \delta_{\text{A}} + m_{\text{e}} D_{\text{Ie}} \delta_{\text{e}}) - h_{\text{A}} \frac{n^{2}}{\rho} (m_{\text{I}} D_{\text{AI}} \delta_{\text{I}} + m_{\text{e}} D_{\text{Ae}} \delta_{\text{e}}) - h_{\text{e}} \frac{n^{2}}{\rho} (m_{\text{A}} D_{\text{eA}} \delta_{\text{A}} + m_{\text{I}} D_{\text{eI}} \delta_{\text{I}}) \right] + \left[nkT \left(\frac{D_{\text{A}}^{T} \delta_{\text{A}}}{n_{\text{A}} m_{\text{A}}} + \frac{D_{\text{I}}^{T} \delta_{\text{I}}}{n_{\text{I}} m_{\text{I}}} + \frac{D_{\text{e}}^{T} \delta_{\text{e}}}{n_{\text{e}} m_{\text{e}}} \right) \right]$$
(12)

where λ_t is the translational thermal conductivity, the sum of all terms containing the various h_i 's is the reactive thermal conductivity, and the sum of the remaining terms is the thermal conductivity due to thermal diffusion. Note that the reactive component has two modes. The first is by multicomponent diffusion and the second by thermal diffusion. For a fully ionized gas⁵ (i.e. no neutral particles) eq (12) reduces to

$$\lambda_{\text{total}} = \lambda_{\text{t}} - \frac{k}{nD_{\text{eI}}} \left(\frac{D_{\text{e}}^{\text{T}}}{\mu} \right)^{2}$$
 (13)

where μ is the reduced mass of the electron-ion system.

Since the terms in eq (12) are so complex it would be impossible to single out by inspection any one mechanism (e.g. thermal diffusion) as being the chief contributor to λ_{r} or λ_{d} . This can be done only by an inspection of the numerical values which are described in the next section. However, it can be seen from eq (12) that there is a definite need for accurate values of the multicomponent and thermal diffusion coefficients since λ_{r} and λ_{d} are determined by Dij and Di, and since δ_{i} (the combined effect of the concentration gradients and the charge separation field) are also determined by Dij and Di (eqs (10) and (11)).

3. Numerical Values of Higher Order Transport Coefficients

The importance of higher order Sonine expansion terms in the expressions for λ_t , D_{ij} , and D_i^T will be described first. The expressions for λ_t , D_{ij} , and D_i^T [10] are the ratio of two determinants. If the first and second Sonine expansion terms are used (second approximation) then both determinants contain four subdeterminants which are designated as the 00, 01, 10, and 11 subdeterminants, where the 0 corresponds to the first Sonine polynomial and the 1 corresponds to the second Sonine polynomial. In the calculation of the thermal conductivity of neutral gases the 00, 01, and 10 subdeterminants are normally discarded (first approximation) with very little loss in accuracy [10]. Unfortunately, this simplification was carried over into the calculation of the thermal conductivity of partially ionized gases. The result of this approximation is shown in figure 3 for partially ionized argon. The second approximation of $\lambda_{
m t}$ [12] is larger than the first approximation by 30 percent at 50-percent ionization and larger by 50 percent at complete ionization. An inspection of the numerical values of the elements in the λ_t subdeterminants [12] show that the increase in λ_t in going from the first to the second approximation can be attributed to the inclusion of additional terms in the 00 subdeterminant arising from interactions between unlike particles (A-I, e-A, and e-I). Subsequent analyses by DeVoto [16 and 17] showed that third order Sonine expansion terms for the translational thermal conductivity were also appreciable. Figure 3 shows that the difference between the third and second approximations for λ_t is roughly the same as the difference between the second and first approximations. DeVoto's calculations, however, show very little difference between the third and fourth approximations. Landshoff's [18] calculations for an electron gas show roughly the same trends in going from the second to the fourth approximation.

⁵The author [12] erroneously identified λ_t with Spitzer's [2] field free thermal conductivity. The error was resolved by the analysis of Meador and Staton.

Multicomponent diffusion coefficients are usually approximated by retaining only the first Sonine expansion terms (i.e. using only the 00 subdeterminant). These first-order coefficients are compared with the second-order coefficients (i.e. both first and second Sonine expansion terms) in figure $^{\downarrow}$. The second-order coefficients $D_{e-A}(2)$ and $D_{e-I}(2)$ are larger than the corresponding first-order coefficients by 25 percent at 50-percent ionization and by $^{\downarrow}$ 5 percent at complete ionization. An inspection of the numerical values of the elements in the $D_{i,j}$ subdeterminants show that the increase in $D_{i,j}$ in going from the first to the second approximation can be attributed to the inclusion of terms in the 11 subdeterminant arising from interactions between like particles (A-A, I-I, and e-e). The electron-electron interaction is especially important since a simple hard sphere model shows that $D_{i,j}$ is inversely proportional to the product of the collision cross section and the reduced mass. In contrast, the first-and second-order coefficients for diffusion between heavy particles (e.g. D_{A-I}) differ by only a few percent. DeVoto's calculations show that there is little difference between second- and third-order multicomponent and thermal diffusion coefficients.

It is essential that second-order thermal diffusion coefficients be used since these coefficients are identically zero in the first approximation. Typical values of the second-order thermal diffusion coefficients for the argon atom, ion, and electron from [11] are shown in figure 5. In the expression for the total thermal conductivity (eq (12)), D_{1}^{m} always occur in combination with the particle mass in the denominator. Although the electron thermal diffusion coefficient, D_{e}^{m} , is at most two orders of magnitude smaller than those for the atom and ion, the electron mass is four orders smaller. Consequently, thermal diffusive effects can be attributed almost entirely to the electron term. Another interesting conclusion can be reached by an inspection of figure 5. It can be seen that the atom and ion thermal diffusion coefficients are within 1 percent of each other in magnitude from a few percent ionization up to extremely high degrees of ionization (approximately 95 percent). Beyond this point D_{1}^{m} decreases in value, changes sign, then approaches the value of D_{e}^{m} near 100-percent ionization. These variations imply that the diffusive motion of both the atom and ion are essentially independent of that for the electron, up to large degrees of ionization. The diffusive motion of the electrons, in turn, is dictated by the ion rather than the atom because of the greater magnitude of the Coulombic forces. These same conclusions were reached from an examination of the second-order multicomponent diffusion coefficients.

The previous discussion of second-order values of $D_{i,j}$ and $D_{i,j}^T$ leads towards the calculation of λ_r and λ_d from eqs (10), (11), and (12). The author recently made a series of calculations for hydrogen, nitrogen, and argon for a pressure of one atmosphere and temperatures corresponding to 50-percent ionization. The values of λ_r were compared with those based on the expressions derived by Meador and Staton [15]. The values of λ_r from the two sets of calculations agreed within a few percent. However, this is not necessarily a verification of the Meador and Staton approach, as calculations have shown that any non-trivial assumed values of $\partial_{x_1}/\partial_r$ and $\partial_{x_e}/\partial_r$ will result in the same values of λ_r and λ_d . The agreement can be explained as follows. The values of λ_r and λ_d are determined not by the separate effects of the concentration gradients and the charge separation field, but by their combined effects. Consequently, if erroneous values of the concentration gradients were initially assumed the constraints of the problem (eqs (5), (6), and (8)) would compensate for this error in the resulting value of the charge separation field.

A more critical comparison could come from the determination of the predominant mechanism for the reactive component of the thermal conductivity. The reactive component from eq (12) can be resolved into two components: (1) the sum of the $h_i n^2 m_j D_{i,j} \delta_j / \rho$ terms which shall be called the $D_{i,j}$ component for identification, and (2) the sum of the $h_i D_{i,j}^T / m_i T$ terms which shall be called the $D_{i,j}^T$ component. The results are summarized in the following table.

Table I. Th	ermal Conductivit	y Components	for Partiall	y Ionized Gases	(p = 1 a.tm)	, 50% ionization)
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	Դ _ቲ (2)	λ _r (2) W m	λ _d (2)	
Gas	W m ⁻¹ deg ⁻¹	D _{ij} component	$ extstyle{D}_{f i}^{ m T}$ component	W m ⁻¹ deg ⁻¹
Hydrogen	1.30	5 • 77	1.78	- 0.20
Nitrogen	1.34	0.87	1.30	- 0 . 25
Argon	1.31	-0.17	1.32	- 0 . 29

 $^{^{6}}$ As a result, the values of D_{e}^{T} calculated for partially ionized argon can be used for other partially ionized gases to a good degree of accuracy.

For hydrogen the largest contribution comes from the $D_{i,j}$ component, and the predominant term in this component is the h_T n maDTASA/ ρ term as predicted by Meador and Staton. However, the thermal diffusive contribution is not negligible, but comprises 25 percent of the value of λ_r . As the mass of the heavy particle increases, thermal diffusive effects become relatively more important. For example, in nitrogen the D_1^T component of λ_r is larger than the $D_{i,j}$ component. In argon the $D_{i,j}$ component is almost zero due to the cancellation of the ion term by the atom and electron term. Consequently, the reactive thermal conductivity for argon can be attributed almost entirely to the D_2^T component, and the predominant term in this component is the $h_eD_e^T/m_eT$ term. This result is in direct contradiction to those predicted by Meador and Staton and indicates that one or more of their initial assumptions may be erroneous.

This paper has described the analytical work done in the past few years to clear up some of the uncertainties in the expression for the total thermal conductivity of a partially ionized gas. The author feels that the theoretical basis for this expression is currently on substantial ground. However, there are several deficiencies which must be resolved before accurate values can be calculated. The first of these is the lack of measured or calculated cross sections for collisions between an atom which is chemically unstable at low temperatures (e.g. nitrogen or oxygen) and an electron, ion, or another chemically unstable atom. A second deficiency is the absence of terms in the expressions for the transport coefficients which account for inelastic collisions, and the lack of measured or calculated cross sections for these inelastic collisions. A third deficiency is the absence of any experimental verification of the total thermal conductivity, especially in the region of 50-percent ionization where λ_{total} peaks because of the reactive component. A method which shows some promise is the ultrasonic absorption technique as used by Carnevale et al. [19]. Consequently, large amounts of analytical and experimental effort must still be expended to remedy these deficiencies before accurate values of the total thermal conductivity of a partially ionized gas can be obtained.

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FIGURE LEGENDS

- Figure 1.- Comparison of experimental and theoretical electrical conductivity of nitrogen.
- Figure 2.- Comparison of experimental and theoretical electrical conductivity of argon.
- Figure 3.- Comparison of various approximations for calculating the translational thermal conductivity of argon.
- Figure 4.- Comparison of various approximations for calculating multicomponent diffusion coefficients of argon.
- Figure 5.- Thermal diffusion coefficients of argon.

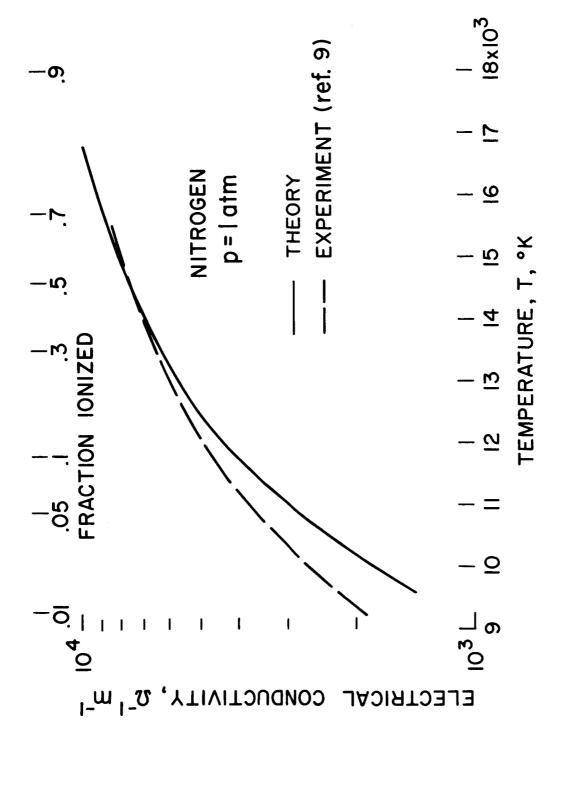


Figure 1.- Comparison of experimental and theoretical electrical conductivity of nitrogen.

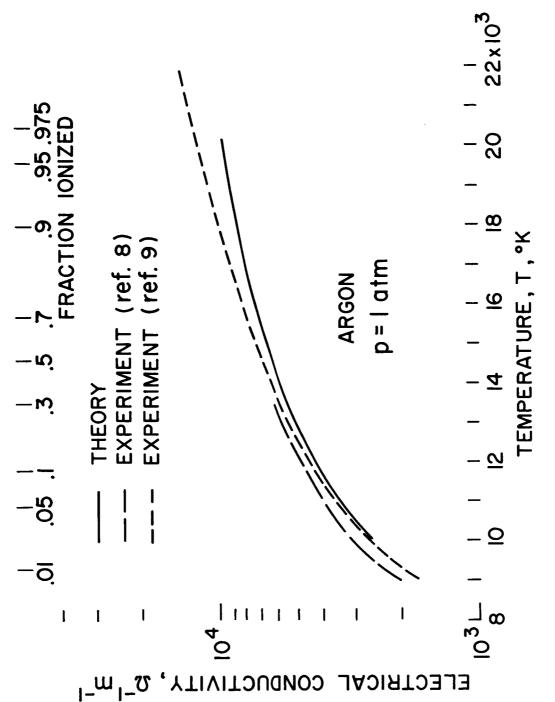


Figure 2.- Comparison of experimental and theoretical electrical conductivity of argon.

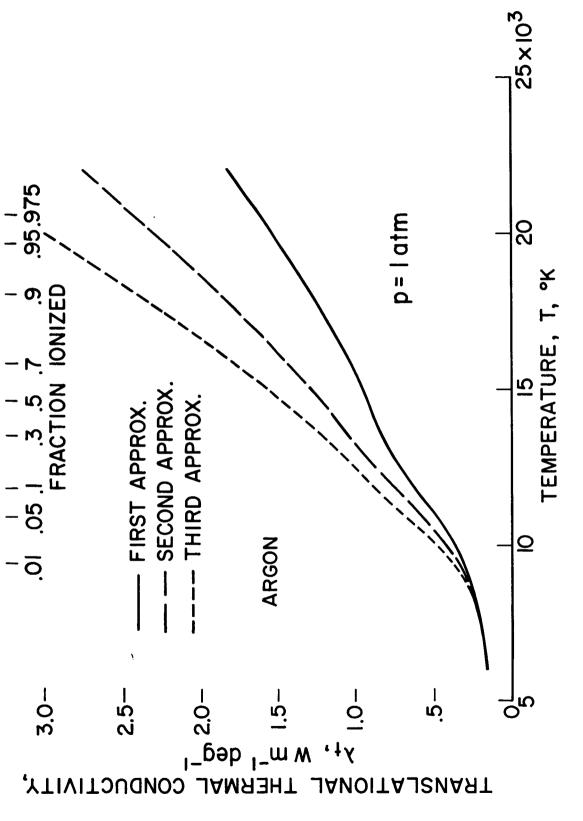


Figure 3.- Comparison of various approximations for calculating the translational thermal conductivity of argon.

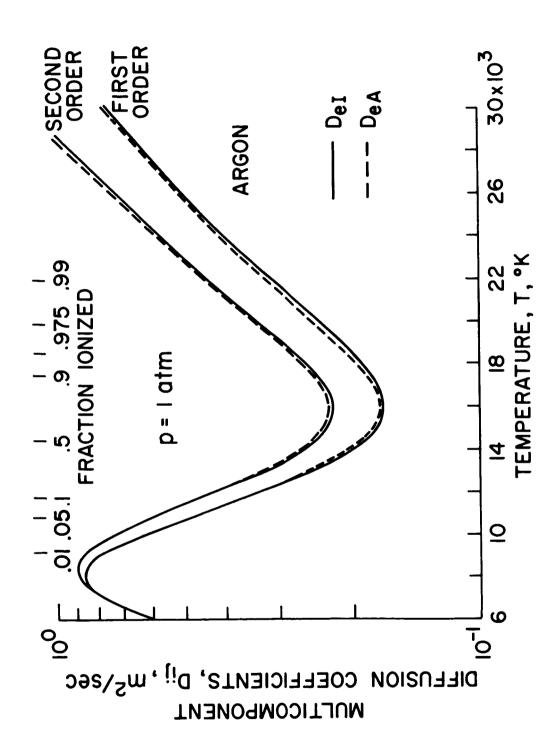


Figure 4.- Comparison of various approximations for calculating multicomponent diffusion coefficients of argon.

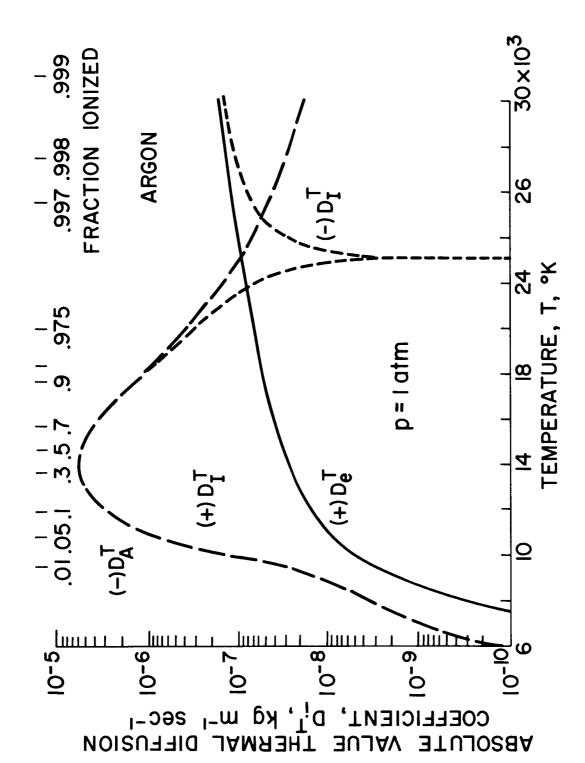


Figure 5.- Thermal diffusion coefficients of argon.